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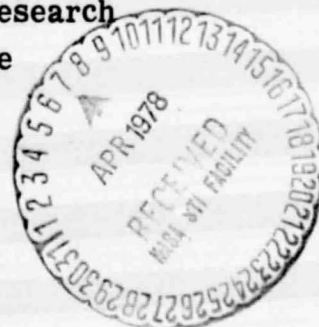
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**DEFINITION AND EFFECT OF CHEMICAL PROPERTIES
OF SURFACES IN FRICTION, WEAR, AND LUBRICATION**

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ABSTRACT

Much of the data relative to the properties of surfaces that have been used in the past in analyzing, interpreting and predicting adhesion, friction and wear behavior for solid surfaces is now suspect. With the advent of analytical surface tools, careful and complete characterization of surfaces indicate that very frequently the outermost layers of solid surfaces are markedly different in chemistry than had been previously thought. These layers, as will be shown, are extremely important in adhesion, friction and wear behavior. Some of the properties to be discussed in the paper relative to their role in adhesion, friction, wear and lubrication will include: (1) adsorption, both physical and chemical; (2) orientation of the solid as well as the lubricant; (3) surface energy; (4) surface segregation; (5) surface versus bulk metallurgical effects; (6) electronic nature of the surface; and (7) bonding mechanisms.

INTRODUCTION

The properties of surfaces are extremely important in the adhesion, friction, wear and lubrication of materials. This fact was recognized by Sir William Hardy¹ over a half a century ago! It has, however, only recently been possible to define and fully characterize these surfaces. The advent of special surface tools has assisted in the characterization.

These include: field ion microscopy (FIM), the atom probe, low energy electron diffraction (LEED), Auger emission spectroscopy analysis (AES), electron spectroscopy for chemical analysis (ESCA), ellipsometry and scanning electron microscopy (SEM).

Through the years from Hardy to the availability of these tools, considerable research has been conducted relative to the physics, chemistry, and metallurgy of solid surfaces, in general, and more specifically as related to tribological systems. In light of the current identification of the real nature of solid surfaces many of the concepts, mechanisms and theories previously held may have to be modified or discarded. This may be particularly true where bulk properties have been used to predict surface behavior.

The objective of this paper is to review the importance of surface effects and the need for a careful definition of solid surfaces in friction, wear and lubrication. While in the past the physicist, chemist, and metallurgist had well defined areas of activity with regard to the behavior of materials it will become evident that the chemistry of surfaces to which this paper is devoted will involve, of necessity, physics and metallurgy. Some of the properties to be discussed in the paper relative to their role in adhesion, friction wear and lubrication will include, adsorption, both physical and chemical, orientation of the solid as well as the lubricant, surface energy, surface segregation, surface versus bulk metallurgical effects, electronic nature of the surface and bonding mechanisms.

REAL SURFACES

Until approximately ten years ago it was very common to find in classical texts on surface chemistry a nearly complete absence of the characterization of solid surfaces with which gases and liquids would interact.² A wealth of literature has been developed through the years concerning adsorption to solid surfaces, particularly chemisorption. Again, very little attention has been paid to the nature of the surface of

the solid involved. Frequently M was used to designate the metal involved where adsorption studies were conducted with metals.^{3,4}

In the field of tribology because of the importance of surfaces the presence of oxides and adsorbates has been recognized.⁵ Despite this recognition it has been a common practice to consider solid surfaces, which are usually metals, as reacting directly with the lubricants, indicated by way of example in References 6 to 10. Frequently metal powders, particularly iron have been used as the adsorbing surface for the lubricant.^{6,7} Metal powders have, however, been identified as being poor relative to gas adsorption; they are poor with respect to both surface cleanliness and characterization.¹¹ The same may be said with regard to liquids.

If the surface of high purity iron (vacuum zone refined) is examined with Auger emission spectroscopy it is found to contain more than simply iron as indicated in Fig. 1(a). In Fig. 1(a) in addition to iron, oxygen, carbon, and sulfur are detected on the surfaces. These elements are stable on the surface and resist techniques such as heating to 500^o C to achieve their removal. The only method found effective in accomplishing the removal of all the extraneous elements was argon ion bombardment.

Figure 1(b) is an Auger emission spectrum for the iron surface after argon ion sputter cleaning. The only element detected is iron. The surface atoms of the iron however been strained by the ion bombardment. If the clean iron surface is then heated to 500^o C to anneal the surface, carbon from the bulk diffuses to the surface and contaminates the surface. A LEED pattern is presented in Fig. 2(a) for this surface.

In Fig. 2(a) the four brightest spots in a rectangular array are due to the iron (011) crystal surface. The diffuse and less intense spots appearing in a circular pattern are due to the carbon contamination. The Auger spectrum of Fig. 3 indicates that the surface contaminant is carbon.

The removal of the carbon by argon ion bombardment results in the LEED pattern of Fig. 2(b). The diffraction spots are diffuse and elongated. A very modest heating at 200^o C for a very short period of time

results in the LEED pattern of Fig. 2(c) for the clean annealed iron (011) surface.

The interaction of even the simplest of elements with the clean iron surface becomes very involved and must be carefully followed to understand the mechanism of interaction. This is accomplished with the aid of surface analytical tools. It has been very effectively done in the study of the chemisorption and chemical reaction of oxygen with iron.¹²⁻¹⁴

The surfaces of most metals are not too different from that observed for iron and usually there are a number of elements present on the surface in addition to those of the metal. The role of these elements on the interaction of lubricants with the solid surface is not fully understood but some of these reactions will be discussed later in reference to gas-solid surface interactions.

SURFACE ENERGY

If one cleaves a crystalline solid along its cleavage plane, two highly chemically active surfaces are generated. The cleavage process causes the fracture of cohesive bonds across the cleavage interface and these fractured bonds leave the surface in a highly energetic state. The energy of the surface will be dependent on both the elemental nature of the bonds broken and the coordination number of the atoms in the resultant two surface layers. As a result, surface energy will be a function of the material¹⁵ as well as the surface orientation.¹⁶⁻²¹

There is no question but that surface energy is important in the tribological behavior of materials. It will influence adhesive bonds for solids in contact and hence friction and adhesive wear. In addition it will determine the nature of the interaction of lubricants with solids. The lubricant may either: (1) physically adsorb; (2) chemisorb; or (3) undergo decomposition, as has been observed for some hydrocarbons with a clean metal surface.²² Surface energy has been used in the formulation of an adhesive wear mechanism.²³

While surface energy can be very helpful in understanding the adhesion friction, wear and lubrication behavior of materials, its present

usefulness is very limited. The principle restriction has been the inability to obtain accurate experimental surface energy values.

An examination of the surface energy literature reveals wide disparities in reported values for any one material. Table I indicates the minimum and maximum surface energy values which can be found in the literature for some of the elemental metals. These data were taken from a summary by Wawra.¹⁵

While the broad range of values obtained are of concern, the fact that, for example, the minimum to maximum for some metals such as iron and chromium fall within the range found for tungsten are of even greater concern. It would, be difficult, based upon reported experimental data, to identify differences in the surface energy for iron, chromium and tungsten.

As has already been indicated, the surface energy of solids such as metals is sensitive to crystallographic orientation. Most researchers conversant in the subject of surface energy readily agree that this is the case. Differences arise, however, when actual results are compared. The research results of three different investigators who have measured the surface energies for various planes of face centered cubic metals are presented in Table II. The results are presented as the ratio of the surface energies for the various planes over that for the (111) surface.

The results of Table II indicate that not only does the value vary with the investigator but more importantly the relative, order of the metals as well.²⁴

One of the most significant reasons for the wide disparity in the surface energy values reported by various investigators has been inadequate control over the impurities in the materials. Small concentration of impurities in the bulk of a metal can markedly alter the measured surface energy of a material. This is indicated in the data of Fig. 4 for sulfur in iron. With an increase in concentration of sulfur, there is an accompanying decrease in surface energy, Fig. 4.

Extremely small concentrations of bulk contaminant in a metal such as iron can have a pronounced effect in contaminating a surface. For example, as little as 8 ppm of carbon in iron will diffuse to the surface,

segregate there and contaminate it.²⁵ This segregation will undoubtedly affect measured surface energies.

The use of high purity materials and the careful characterization of solid surfaces should result in the future acquisition of meaningful surface energy values. Surface analytical tools are currently being used for the needed surface characterization. One which has proven especially useful in this regard is the field ion microscope.^{20, 26, 27} When used in conjunction with the atom probe, its contribution will be enhanced. It gives the atom by atom structural arrangement on a solid surface and with the atom probe an atom by atom chemical analysis.

ALLOY CHEMISTRY

In practical lubrication systems the mechanical components in solid state contact are most frequently alloys rather than elemental metals. The composition of these alloy surfaces are important in considering the chemical interactions of such solids with other solids, with gases and with lubricants. Even where elemental metals are used, the surfaces of these metals may have compositions entirely different from the bulk which results from impurity segregation.

The field of tribology contains a number of excellent texts. Many of these books do not, however, discuss the real nature of the surface to be lubricated (see, for example, Refs. 23, 28, 29 and 30). Much attention is given to the chemistry of the lubricant but little to the chemistry of the alloy surface to be lubricated. In fairness to the authors of these texts the identification of these surfaces with surface tools just began to emerge at the time these texts were written. Future texts on the subject should, however, not neglect the importance of the metal or alloy surface chemistry and the interaction of the lubricant with that surface chemistry.

With elemental metals, the effect of small concentrations of impurities such as parts per million carbon in iron have been shown to affect surface chemistry. This was discussed earlier in this paper. Similar effects have been observed with other impurity elements in a number of

different metals. Surface segregation has been noted for oxygen in platinum,³¹ phosphorus in iron,³² sulfur and carbon in nickel,³³ sulfur in molybdenum,³⁴ carbon in nickel,³⁵ and even sodium in lithium.³⁶

The foregoing are only examples, other impurity effects have been studied and still other systems, it is certain, will be studied. With some of these impurities the metal surface is completely covered by the contaminant which can diffuse from the bulk and even form compounds with the metal itself at the test surface. These compounds do not exist in the bulk.³⁴

In lubrication systems, the rubbing off of surface oxides and adsorbates because the solid surfaces are in contact under relative motion is a common occurrence. Frictional heating of the surface layers can promote the diffusion of impurities to the surface under such conditions. The presence of impurities in metals is therefore important to surface chemical behavior of the materials in solid state contact. A foreign atom which may simply be an impurity in the bulk can be an alloy constituent of the surface or compound with it.³⁴

When elements are alloyed, the segregation of one element to the surface can occur and its concentration at the surface can exceed that in the bulk alloy. Thus, for a given alloy the surface metallurgy can differ appreciably from the bulk metallurgy. Such surface enrichment has been observed with a host of systems. A few examples of such systems include nickel in iron,³⁷ silver in palladium,³⁸ gold in copper,³⁹ copper in nickel,⁴⁰ silver in gold,⁴¹ aluminum in copper,⁴² tin in copper,⁴³ aluminum in iron,⁴³ and platinum in osmium.⁴⁴

The amount of material which can be present on the surface of alloys relative to the bulk concentration of the alloying element can be appreciable. This is indicated in the data of Table III for aluminum and tin segregating to the surface of copper and aluminum to the surface of iron. The surface concentration ranges from approximately 3 to 15 times the bulk concentration of the alloying element.

One theory relevant to the reason for the segregation of the solute to the surface of the solvent metal is that involving lattice strain. It has been postulated that if the solute atom is larger in size than the solvent

atom, it will strain the solvent lattice and therefore there exists the tendency to squeeze the solute out of the solvent lattice. From the atomic sizes presented in Table VI it appears that the experimental results agree with the theory. Still another theory involves the concept of surface energy reduction. The difficulties in using surface energies has, however, already been discussed.

Surface segregation of alloy constituents has a very definite effect upon the adhesion, friction, wear and lubrication of alloy surfaces. The effect on the adhesion of copper base alloys can be seen in the data of Fig. 5.

In Fig. 5 a fivefold increase in the adhesion of copper occurs with the addition of as little as one atomic percent aluminum. Further increases in the aluminum concentration beyond one percent do not produce any further change in adhesion behavior. In fact, the adhesion data for pure aluminum in Fig. 5 is approximately the same as that obtained for the copper containing one atomic percent aluminum. The data of Fig. 5 were all obtained with metal and alloy single crystals having a (111) surface orientation in order to eliminate orientation as a possible variable.

Both LEED and Auger emission spectroscopy were used to identify the segregation of the aluminum to the copper surface. The surface structure resulting from this identification is presented in Fig. 6. From an examination of Fig. 6 it can be seen that the outermost layer of the solid consists of a layer of aluminum atoms. The density of aluminum atoms in this layer will vary with bulk concentration but the layer is always aluminum. It is for this reason that no difference in adhesion behavior was detected from one atomic percent to pure aluminum.

The presence of some alloying elements can, upon segregation, promote surface chemical activity and thereby adhesion. Such behavior was observed for aluminum in copper while with other elements chemical surface activity and adhesion are reduced. Such a reduction effect is observed for tin in copper.⁴³

If an alloy of tin (one atomic percent) in copper is sputter cleaned, the adhesion behavior of the alloy is comparable to that for pure copper as indicated in the data of Fig. 5. The reason for this is that sputtering

removes the surface segregated tin. Heating, however, to 200° C causes the tin to segregate at the surface and brings about a reduction in adhesion (Fig. 5).

Among ferrous base alloys, both aluminum⁴³ and silicon⁴⁵ have been found to segregate to the surface of iron. Aluminum in iron segregates to the surface and increases adhesion. It also causes, in the clean state, an increase in friction and wear over that observed for iron without aluminum.⁴⁶ Alloy surface chemistry is therefore important to friction and wear as well as adhesion. It should be indicated that, while increased surface chemical activity of the aluminum-iron alloy produces an increase in adhesion, friction and wear for dry metal contact, it also results in increased activity with lubricants which can be beneficial.⁴⁶

Silicon alloyed with iron behaves in a rather unusual manner. If a silicon-iron alloy is heated, silicon will segregate to the surface.⁴⁵ When, however, the alloy is cooled to room temperature the silicon returns to the bulk. It is a reversible segregation. This is unlike the behavior of other alloy systems where the segregation is irreversible. If, however, the silicon is allowed to react with oxygen while on the surface the formation of silicon oxide prevents the return of the silicon to the parent lattice from which it came.

In Fig. 7 friction coefficient is plotted as a function of oxygen exposure for iron and for an iron 3 1/2 percent silicon alloy. Prior to the admission of oxygen, the friction coefficient is extremely high for the alloy and the pure iron seizes completely. As the surfaces are exposed to oxygen, the friction for both the alloy and the elemental iron decrease. This decrease occurs, however, much more rapidly for the alloy than for the iron. The difference is due to the segregated silicon and its interaction with oxygen at the surface. The sliding process is capable of generating sufficient frictional heating to cause the silicon to segregate at the alloy surface. Auger analysis confirmed its presence.⁴⁵

GAS-SOLID INTERACTIONS

Specie and Concentration

Almost all surfaces involved in tribological systems, with the exception of those operated in a good vacuum (e. g. , 10^{-10} torr), are exposed for interactions with gaseous constituents of the environment. This is true for lubricated as well as unlubricated systems.

Oxygen is probably the best "lubricant" available. It will reduce friction coefficients for clean metals from complete seizure to values of less than 1.0 (See data of Fig. 7). Liquid lubricants will reduce the dry sliding value from less than 1.0 to a value of approximately 0.1.

Extremely small concentrations of surface films can influence adhesion and friction. For example, fractions of a monolayer of adsorbed oxygen or chlorine on a clean iron, copper or steel surface will reduce static friction as seen from the data of Fig. 8. In Fig. 8 static friction is plotted as the inverse of surface coverage to the point where the surface is covered by a monolayer.⁴⁷ From these data the importance of gas-solid interactions at the surface of the solid is readily apparent.

Interaction Mechanisms

There are three basic types of interactions between a gas and solid surface: (1) physical adsorption; (2) chemisorption; and (3) chemical reaction. Physical adsorption involves weak bonding forces (van der Waals) and are not specific. Because of the highly energetic state of clean metal surfaces it is seriously doubted that such adsorption occurs on these surfaces other than with inert gases. The forces involved are comparable to those involved in liquification.⁴⁸

Chemical adsorption or chemisorption involves very strong chemical bonds, comparable to those for chemical reaction and further are highly specific. They play a very important role in adhesion and friction as indicated in the data of Fig. 8.

Great care must be taken in using chemisorption data which appears in the literature. The current use of surface tools in the study of adsorp-

tion has indicated that earlier findings are incorrect in many instances. For example, earlier studies have indicated that gold does not chemisorb oxygen.⁴⁹ More recent studies have, however, with the aid of LEED and AES analysis, indicated that gold in fact does chemisorb oxygen.^{50, 51} Ref. 49 indicates that nitrogen does not chemisorb to platinum while Ref. 52 reports that it does. The reason for the earlier study not observing adsorption of nitrogen to platinum can be found in Ref. 52. Nitrogen adsorption becomes significant only after any carbon contamination is removed from the platinum surface by heating in oxygen and removing the CO that forms from the system. Such results indicate the importance of using analytical surface tools to characterize the adsorbing surface.

Orientation of Solid

Adhesion and friction are extremely sensitive to surface character as already indicated. With various adsorbed gases, friction is not only a function of the adsorbed gas but the surface orientation as well. In Tables IV and V friction coefficients are presented for various gases chemisorbed to three different atomic planes of tungsten (See data for oxygen and hydrogen sulfide, Table IV).

An examination of Table IV indicates that even hydrogen will reduce the friction of tungsten. This occurs on all three planes of tungsten with only the magnitude of the reduction varying with the plane. Oxygen is more effective than sulfur in reducing the friction of tungsten.

Molecular Structure

The data of Table V indicates that even the degree of bond unsaturation with hydrocarbons has an effect on friction. The greater the degree of bond unsaturation, the lower the friction coefficient for any given plane. It is difficult to interpret these results in light of adsorption mechanisms proposed for the adsorption of these gases to a tungsten surface. For example, with the adsorption of ethylene whether the adsorption is a single or two step decomposition process is in dispute.⁵²

Disagreement exists even as to the mechanism for the adsorption of the simple hydrocarbon methane to a tungsten surface.⁵³ Hopefully future surface studies with well characterized surfaces will resolve this conflict.

From the data of Table V there is no question that what is present on the tungsten surface varies either in composition or structural arrangement, otherwise friction differences would not be observed. This is true not only with the adsorption of the various gases on a single plane but with different planes of tungsten as well.

Much of the difficulty in attempts to study adsorption of gases, and liquids as well, to solid surfaces is the pronounced effect small concentrations of bulk impurities can have on the surface. This is true with metals such as tungsten and even more so with metals like iron. Concentrations of 10-100 ppm of carbon, nitrogen or sulfur in bulk iron will segregate to the surface and will have an effect.⁵⁴ When gases are adsorbed to well characterized iron, pronounced tribological effects are seen.

Frictional Energy Effects

An area to which very little attention has been paid is the effect of the interfacial frictional energies of two surfaces in rubbing contact on gaseous adsorption. Some studies by the present author indicate that there is an effect but it is a function of the chemistry of the adsorbate. For example if methyl mercaptan is adsorbed onto a clean iron surface in the presence and absence of sliding, differences in the quantity of sulfur adsorbed are observed. These differences are indicated in the Auger spectroscopy data of Fig. 9.

More sulfur is observed on the iron surface in the absence of sliding (Fig. 9). Frictional heating at the interface can promote desorption of the sulfur; this and wear could account for the lesser amount of sulfur observed with sliding. These data indicate that care should be taken in applying static adsorption results to tribological systems.

If sulfur dioxide is adsorbed to a clean iron surface either in the presence of or in the absence of sliding, no difference in adsorption be-

havior is observed. The Auger spectroscopy data of Fig. 10 indicate the same surface concentration of sulfur and oxygen under both conditions.

The data of Fig. 9 indicate a sensitivity of adsorption to rubbing with methyl mercaption while the data of Fig. 10 indicate an absence of such sensitivity. If sliding in Fig. 9 causes desorption of sulfur, then oxygen bonded to the sulfur must assist in resisting desorption, Fig. 10. This implies stronger bonding of oxygen to iron than exists for sulfur to iron.

The relative stabilities of sulfur and oxygen on an iron surface can be demonstrated with the aid of the data from Fig. 11. The data of Fig. 11 were obtained in experiments in which a well characterized clean iron surface was first exposed to 10,000 langmuirs of hydrogen sulfide by the present author. The hydrogen sulfide dissociatively adsorbs on the iron surface leaving a surface saturated with a sulfide film. If that surface is then exposed to oxygen, the oxygen will nearly completely displace the sulfur. This phenomena of displacement is evidenced by the data of Fig. 11.

An oxidized iron surface was exposed to hydrogen sulfide. Sulfur did not displace the oxygen on the iron surface. Thus, from these results one could infer that iron oxide is more stable than is iron sulfide. It should be indicated that the oxide is thermodynamically unstable relative to the sulfide in hydrogen sulfide when no oxygen is present but the activation energy hump must be overcome.

Effect of Mechanical Parameters

Mechanical effects other than simply sliding of the surfaces can have an effect on adsorption and correspondingly on such tribological properties as friction behavior. For example, increasing loads for surfaces in solid state contact as well as increasing sliding velocity between such surfaces will increase the generated interfacial energy. It is reasonable to assume that such changes in energy will alter adsorption behavior.

Sliding friction experiments were conducted by the present author in which an iron surface containing a normal surface oxide was operated

in a vinyl chloride atmosphere at a pressure of 10^{-6} torr. In a series of experiments, the load was increased and both friction force and Auger peak intensities for chlorine monitored. The results obtained are presented in Fig. 12.

An examination of Fig. 12 indicates that the concentration of chlorine in the wear contact zone is a function of load. Chlorine concentration first increases with load as the friction coefficient decreases. An optimum surface coverage is achieved at which point the friction coefficient is at a minimum. Beyond this point surface coverage by chlorine decreases and this decrease is accompanied by a corresponding increase in friction coefficient.

Very little wear occurs to the surfaces presented in Fig. 12. The concentration of chlorine at the surface is 10^{-6} torr and consequentially corrosion or corrosive wear is not involved.

A considerable amount of data in the literature dealing with adsorption of lubricating species to solid surfaces are the result of static exposures. More data on the dynamic interfacial effects on adsorption are needed.

LIQUID-SOLID INTERACTIONS

In lubrication systems the liquid to solid interface and the chemical interactions that take place at the liquid to solid interface are extremely important. As a consequence considerable research has been expended in understanding these interactions. The adsorption of liquids and the effects of hydrocarbon chain length, functional groups, etc., were explored back at the time of Hardy.

An area which has been neglected by the tribologist is the effect of surface liquids on the mechanical behavior of solids. The materials scientist is very familiar with these effects. For example, some surface films produce mechanical strengthening of surface layers of the solid while other produce weakening or softening.⁵⁵ These effects must play a role in the behavior of mechanical components of tribological systems.

Figure 13 illustrates surface effects in a typical stress-strain diagram. With certain surface films (e.g., oxides) a surface mechanical strengthening occurs called the Roscoe effect because it was first observed by him in the strengthening of cadmium crystals by its oxide.⁵⁶ In contrast the presence of certain liquids on the surface of solids produce a softening effect. Many of these liquids are lubricants (e.g., oleic acid).⁵⁷ Rehbinder observed this surface softening on many solids in a number of different liquids and it is therefore called the Rehbinder effect.

From the stress-strain curves of Fig. 13 it is apparent that surface chemistry can influence the mechanical behavior of solids. Films such as oxides can strengthen the material while certain lubricating types of films can increase plasticity. Such effects are important and should not be overlooked in attempting to understand lubricated systems. These effects are demonstrated in Fig. 14 with data from friction and wear experiments.

The data of Fig. 14 are from friction and wear experiments in which films were examined on the surface of the basal (0001) plane of a single crystal of zinc. Three surface states of the zinc were studied, a clean surface generated by cleavage in liquid nitrogen, an oxidized surface and a cleaved surface containing a layer of 5 percent hydrochloric acid in water. The cleaved clean surface would be analogous to the normal surface of Fig. 13, the oxidized surface, strengthening by the Roscoe effect and the acid solution would be a manifestation of the Rehbinder effect of Fig. 13.

The friction coefficient as a function of load in Fig. 14 is greater for the oxidized surface than it is for the surface lubricated with the acid film. These results are as might be anticipated because, in a sense, the acid layer is a lubricant. Chemical reactions with the surface leads to the formation of zinc chloride.

The wear track widths are presented in Fig. 14 for all three surface states. These and the friction results were obtained some years ago by the present author.⁵⁸ The greatest amount of surface deformation occurred with the acid solution, the substance which produces surface softening (Rehbinder effect).

The clean, "as cleaved" crystal surface produced intermediate amounts of surface deformation with the least surface deformation taking place in the presence of the surface oxide. Thus, surface chemistry is important in the mechanical behavior of tribological surfaces.

The mode of deformation as well as the amount is affected by the presence or absence of surface films. In Fig. 15 the zinc single crystal surfaces are examined after sliding experiments with hexadecane present on the surface. Figure 15(a) is for the surface without an oxide layer preformed and Fig. 15(b) is the wear track generated in the presence of an oxide film. Without the oxide, deformation is completely plastic via slip. When the oxide is present deformation twinning is observed as shown in the photomicrograph of Fig. 15(b). A "ladder" of deformation twins is detected in the wear track of Fig. 15(b). These twins are completely absent in Fig. 15(a).

SOLID-SOLID INTERFACE

The surface chemistry and bonding across an interface for two solids in contact is extremely important in understanding the adhesion, friction and wear behavior of materials. With metals and alloys, the materials which have received the greatest attention with respect to chemistry, various properties have been found to affect their surface chemical activity. Such properties include: (1) crystal structure; (2) crystal orientation; (3) solid solubility; (4) surface segregation; (5) surface energy; and (6) d bond character.

Crystal Structure and Orientation

The manner in which metallic atoms bond to one another in the bulk will determine the crystal structure that results. Interfacial bonding of hexagonal metals generally results in strong bonding at the interface but easy shear along basal planes which allows for limited growth in the real contact area, low adhesive bonding forces (because of easy separation along basal planes) and low friction.⁵⁹

Crystallographic orientations at metal surfaces are extremely important in surface chemistry and in solid to solid interactions. Generally in any crystal system (e.g., C.P.H., F.C.C. or B.C.C.) the high atomic density planes are the low surface energy planes and correspondingly the least chemically active. Thus, when {111} planes are brought into contact for face centered cubic metals the adhesive bonding is less than when two {110} planes are brought into contact. Likewise, with hexagonal metals, bonding is weaker between {0001} planes than it is between {1010} planes. This orientation influences bonding effects, adhesion, friction, and adhesive wear.⁵⁹

The foregoing discussion applies to metals in clean solid state contact. When a metal is adsorbed on a solid surface of the same metal the same interaction characteristics exist. Thus, for example, the bonding energy for tungsten adatoms is less on the (110) plane than it is for the (111) plane.⁶⁰⁻⁶¹ In Ref. 60 it is 121 kcal g atom⁻¹ for the (110) plane and 139 kcal g atom⁻¹ for the (111) plane. Similar observations have been made in adhesion and friction studies with tungsten;⁶² that is, adhesive bonding (and correspondingly friction) are less on the (110) than on the less dense atomic planes.

Solid Solubility

Through the years a number of attempts have been made to correlate the solid solubility of metals (bulk) with adhesion, friction and wear of metal surfaces.⁶³⁻⁶⁷ Adhesion, friction and adhesive wear are largely the result of surface properties and consequently surface chemistry, rather than bulk chemistry should be considered. Ample evidence exists to establish differences between surface and bulk bonding of, for example, dissimilar metals.

Tin, copper, and gold are completely insoluble in tungsten.⁶⁸ Despite this bulk insolubility, these elements bond very strongly to the surface of tungsten. With tin, there are two binding energies, a weaker one comparable to the binding energy in bulk tin and a second energy which

is much stronger and occurs in the first monolayer of tin where each tin atom contacts four tungsten atoms.⁶⁰ This bond is unusually strong. With gold to tungsten, the bond is intermetallic in nature at the interface.⁷⁰ Copper alloys with the tungsten surface.⁷¹

Adhesion experiments in the field ion microscope have revealed strong adhesive bonding and transfer of gold to tungsten with surface compound formation.⁷² Adhesion and transfer of copper to tungsten has been observed in sliding friction experiments.⁵⁹

The foregoing caveat against using bulk properties to predict surface behavior not only applies to metal-metal contacts but to metals contacting nonmetals as well. For example, gold has extremely limited solid solubility in both silicon and germanium (less than 10^{-5} atomic percent).⁶⁸ Despite this very limited solubility, gold bonds very strongly to silicon and germanium in adhesion experiments.⁷³

Figure 16 is a photomicrograph of a silicon (111) surface after adhesive contact with gold. Heavy transfer of gold to the silicon is observed. The amount of transfer is greater than is frequently seen for metals in contact with other metals where complete solid solubility exists.⁵⁹ The gold cohesive bonds were weaker than the gold to silicon interfacial adhesive bonds, thus resulting in fracture in the gold.

Strong interfacial bonding was also observed (Ref. 73) for gold to germanium. Separation of the adhesive junction, however, fracture occurred in the germanium rather than in the gold. The cohesive binding energies of gold and germanium are nearly equal. Thus, where the interfacial binding is stronger than the cohesive binding in the elements fracture can occur in either. In the studies, of Ref 73, it take place in the germanium. The cohesive binding energy of silicon, however, is stronger than gold and consequently, fracture occurs in the gold for this particular couple.

The foregoing discussion indicates the importance of avoiding the use of bulk properties to predict surface behavior. On the basis of the solid solubility theory, very little adhesion and transfer should occur for the particular couples discussed yet the opposite result is observed. Conversely, beryllium is soluble in cobalt yet very little adhesive transfer is observed.

Valence Bonding

The importance of surface segregation and surface energy in solid state contacts has already been discussed. The role of d valence bond character of metals on bimetallic adhesion and friction can be useful in predicting friction coefficients for various metals in contact.⁷⁴ This concept gives an indication of the relative amount of electron energy available at a free surface for bonding based on that which is committed to cohesive bonding within the metal itself. Recently, the concept has been applied to metal to nonmetallic bonding, adhesion, and friction of metal to nonmetal couples.⁷⁵

SUMMARY

A critical review of the chemistry of surfaces indicates that much of the interpretation of the data generated in the past may now be suspect because of inadequate characterization of the surfaces. Analytical tools are now available to assist in this characterization. They have already revealed that many metal surfaces do not consist of metallic atoms but rather atoms of bulk impurities which diffuse to the surface and contaminate it. It is now apparent that the wide disparity in the values of surface energy may be a result of these surface contaminants. These surface films are important because even fractions of a monolayer can affect adhesion and friction.

Bulk alloy chemistry can not be extended to the surface because equilibrium segregation will result in a different surface alloy chemistry. The adsorption of lubricating species on the surface of solids is highly specific and not only dependent upon chemistry but orientation as well. Mechanical surface activity influences the adsorption process in some instances and mechanical properties, such as plastic deformation are altered by the presence of adsorbates.

Strong interfacial bonding between dissimilar materials which are insoluble in the bulk occurs and in some instances the bonding and material transfer observed is greater than seen with those materials which

are completely soluble, one in the other. Such observations argue against the use of bulk properties to predict surface behavior.

Adhesion, friction, wear and lubrication are highly dependent upon surface chemistry and, therefore, surface rather than bulk behavior should be used in studying mechanisms which are clearly surface related. Assuming that bulk properties are also surface properties can be very misleading.

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TABLE 1. - VARIATION IN VALUES OF REPORTED
SURFACE ENERGIES*

Element	Surface energy, ergs/cm ²		Temp. , °C
	max	min	
Cu	4258	950	-273
Ag	2493	600	-273
Au	2540	590	-273
Fe	5267	1980	-273
Ti	2730	1330	25, -273
Cr	4061	1515	-273
W	9410	1497	3370

*H. H. Wawra, Radex R. H. , 4(1973)602.

**TABLE II. - STRUCTURAL DEPENDENCE OF SURFACE ENERGY
ON FACE-CENTRED CUBIC METALS**

Plane	Sundquist ¹⁹ Au, Ag, Cu, Ni	Winterbottom & Gjostein ²¹ Au	Mykura ¹⁸ Ni
(111)	1.00	1.00	1.00
(100)	1.047	1.072	0.95
(311)	1.119	1.065	1.00
(110)	1.15	1.047	1.01
(210)	1.16	1.055	1.00

**TABLE III. - MAXIMUM COVERAGE OF MINOR CONSTITUENT
ON ALLOY SURFACES**

Alloy	Ratio of surface concentration to bulk concentration	Atomic size from lattice nearest neighbor distance
Cu-1 a/o Al	6.5	Cu-2.556 Angstrom -f. c. c.
Cu-5 a/o Al	4.5	Al-2.862 -f. c. c.
Cu-10 a/o Al	3.1	Sn-3.022 -Tetragonal
Cu-1 a/o Sn	15.0±2	Fe-2.481 -b. c. c.
Fe-10 a/o Al	8.0	

Note: Atomic size gives a rough measure of the amount that the alloy atom strains the parent lattice.

TABLE IV. - INFLUENCE OF VARIOUS CHEMISORBED GASES ON FRICTION COEFFICIENT TUNGSTEN IN VACUUM*

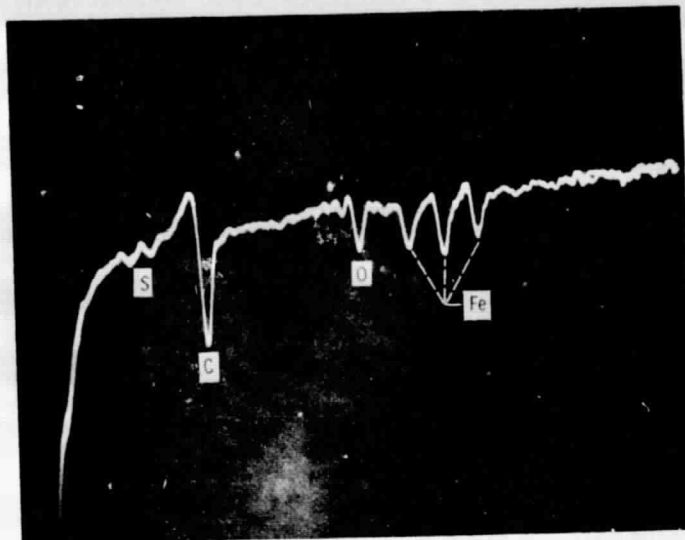
Chemisorbed gas	Coefficient of friction		
	For (110) plane	For (210) plane	For (100) plane
None	1.33	1.90	3.00
H ₂	1.25	1.33	1.66
O ₂	0.95	1.00	1.30
CO ₂	1.15	1.15	1.40
H ₂ S	1.00	----	1.35

*Rider specimen, (100) atomic plane of tungsten; load, 50 g; sliding velocity, 0.001 cm/sec; temperature, 20° C; pressure, 10⁻¹⁰ Torr.

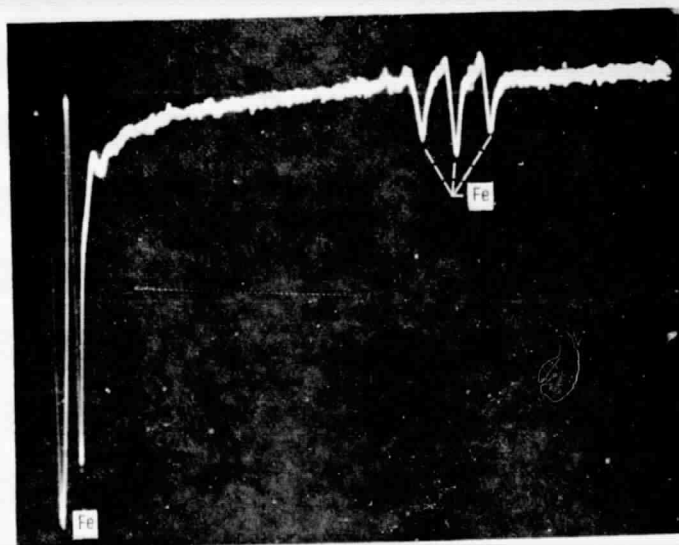
TABLE V. - INFLUENCE OF BOND SATURATION OF CHEMISORBED GASES ON FRICTION COEFFICIENT OF TUNGSTEN IN VACUUM*

Chemisorbed gas	Coefficient of friction		
	For (110) plane	For (210) plane	For (100) plane
Ethane (H ₃ C-CH ₃)	1.10	1.10	1.25
Ethylene (H ₂ C=CH ₂)	0.88	0.85	1.20
Acetylene (HC≡HC)	0.70	0.66	1.00

*Rider specimen, (100) plane of tungsten; load, 50 g; sliding velocity, 0.001 cm/sec; temperature, 20° C; ambient pressure, 10⁻¹⁰ Torr.



(a) Before sputter cleaning.



(b) After sputter cleaning.

Figure 1. - Auger spectra for an iron surface before and after sputter cleaning.
High purity iron vacuum zone refined.



(a) CARBON CONTAMINANTS.



(b) ARGON BOMBARDED.



(c) CLEAN SURFACE (110 V).

Figure 2. - LEED patterns of iron (011) surface with carbon present and after argon iron bombardment.

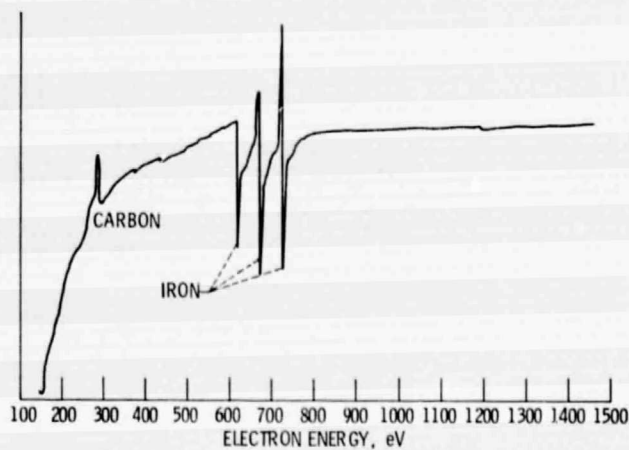


Figure 3. - Auger spectrometer trace of iron(011) surface with carbon present on surface.

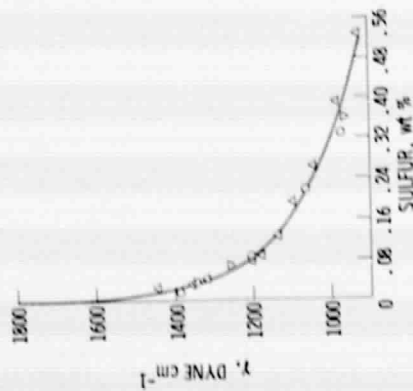


Figure 4. - Dependence of surface energy of liquid iron on sulfur content (ref. 17).

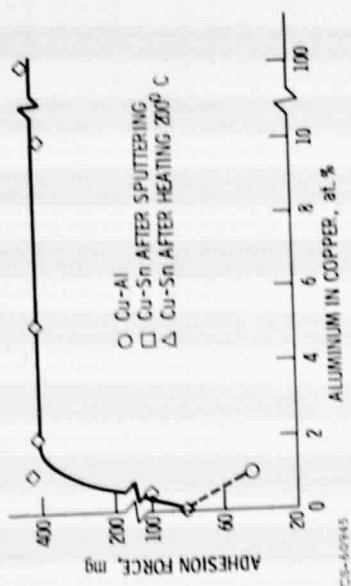


Figure 5. - Adhesive force of (111) gold to (111) surface of copper and copper alloys as a function of bulk concentration.

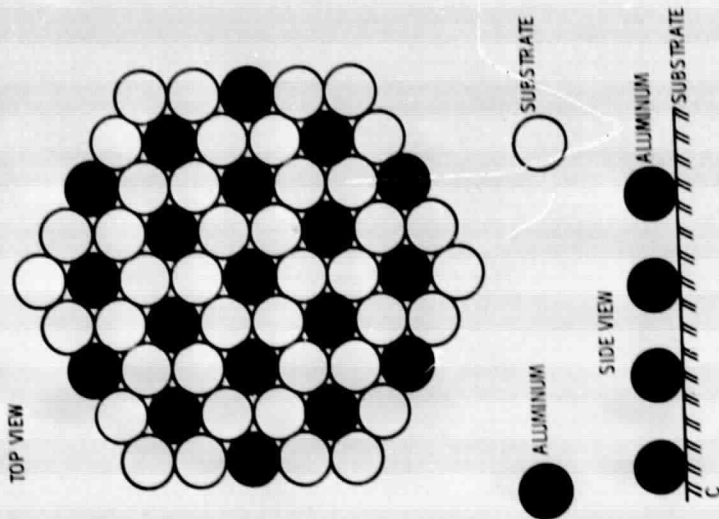


Figure 6. - Surface segregation of aluminum in copper-aluminum alloys.

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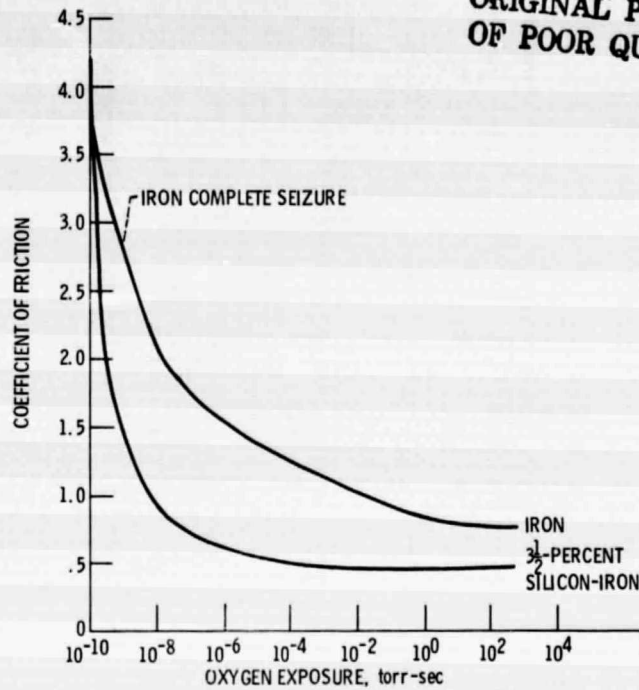


Figure 7. - Coefficient of friction for iron and $\frac{3}{2}$ -percent silicon-iron as function of oxygen exposure. Sliding velocity, 0.001 centimeter per second; ambient temperature, 20°C ; ambient pressure, 10^{-10} torr.

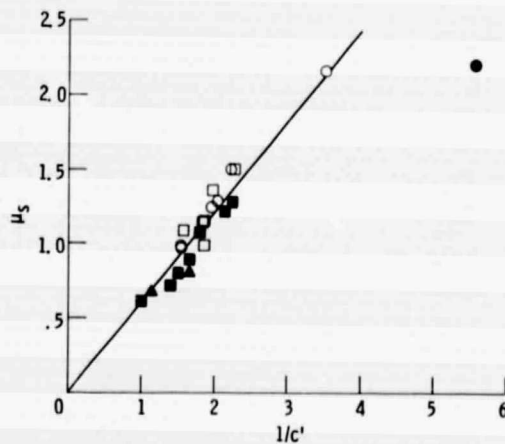


Figure 8. - Static coefficient of friction μ_s as a function of inverse of adsorbate concentration. \circ , chlorine on copper. \square , chlorine on iron. \blacksquare , oxygen on iron. \blacktriangle , oxygen on steel. \bullet , oxygen on copper (minimum μ_s) (ref. 47).

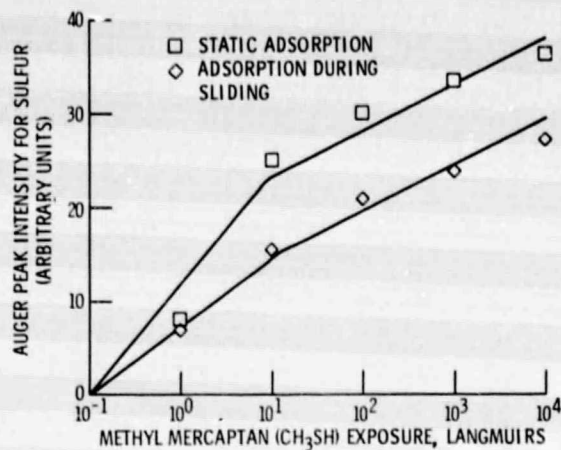


Figure 9. - Auger spectroscopy detection of sulfur adsorbed on a clean iron surface exposed to methyl mercaptan under static conditions and during sliding friction. Sliding velocity, 30 centimeters per minute; load, 100 grams; ambient temperature, 23 C

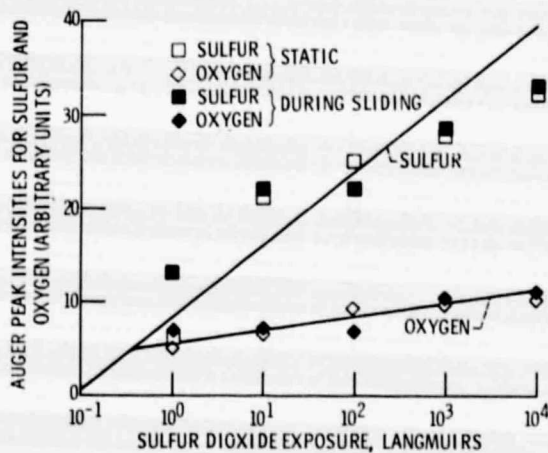


Figure 10. - Auger spectroscopy detection of sulfur and oxygen adsorbed on a clean iron surface exposed to sulfur dioxide under static conditions and during sliding friction. Sliding velocity, 30 centimeters per minute; load, 100 grams; ambient temperature, 23 C.

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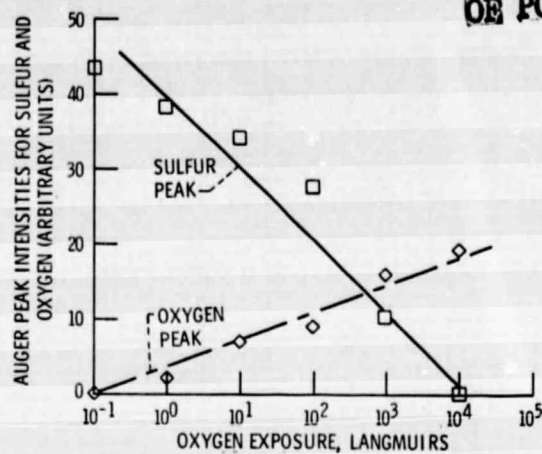


Figure 11. - Auger spectroscopy evidence for the displacement of sulfur from an iron surface by oxygen. Initial sulfide film formed by exposure of iron surface to 10 000 langmuirs of hydrogen sulfide at 23° C.

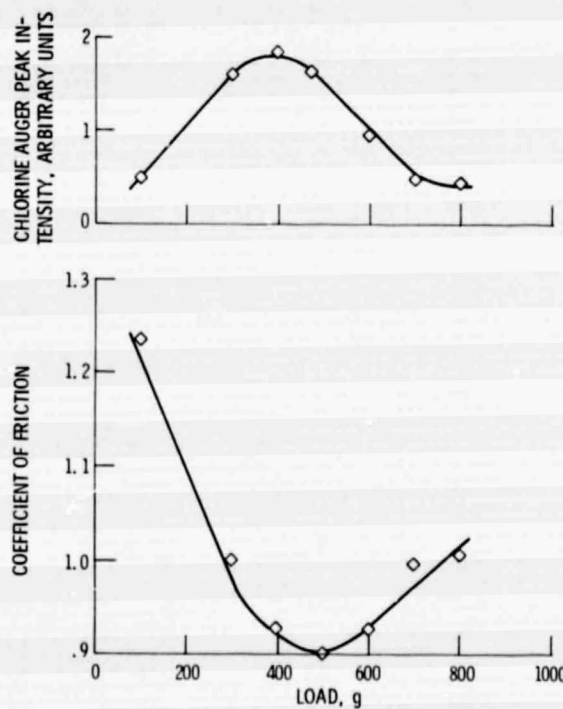


Figure 12. - Coefficient of friction and Auger chloride peak intensity as function of load for vinyl chloride on iron surface. Ambient pressure, 10^{-6} torr of vinyl chloride; rider specimen, aluminum oxide; sliding velocity, 30 centimeters per minute; temperature, 23° C; normal oxides present on iron surface.

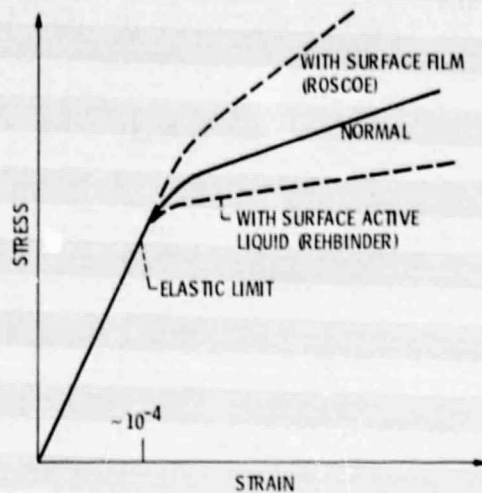


Figure 13. - Schematic illustration of the principal extrinsic surface effects (ref. 55).

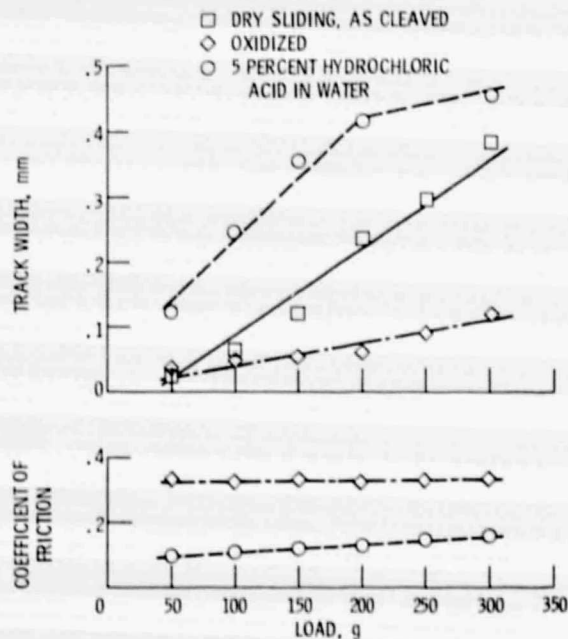


Figure 14. - Width of wear track and coefficient of friction produced with ruby ball sliding on zinc single crystal (0001) surface in $[10\bar{1}0]$ direction. Sliding velocity, 1.4 millimeters per minute; temperature, 23°C ; dry argon atmosphere.

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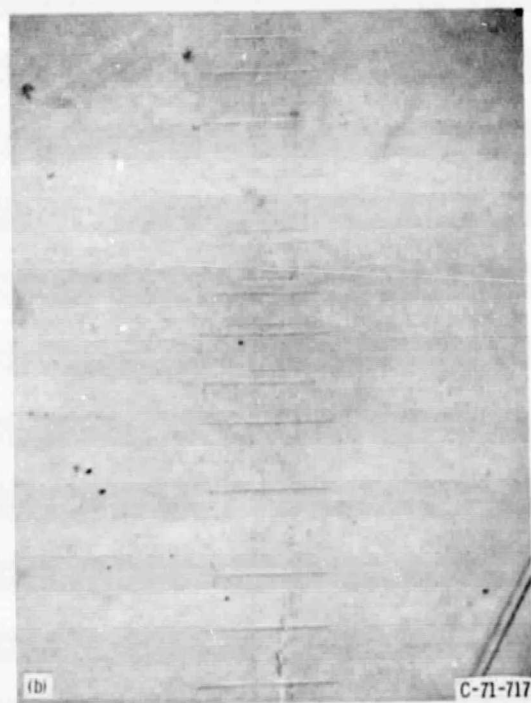
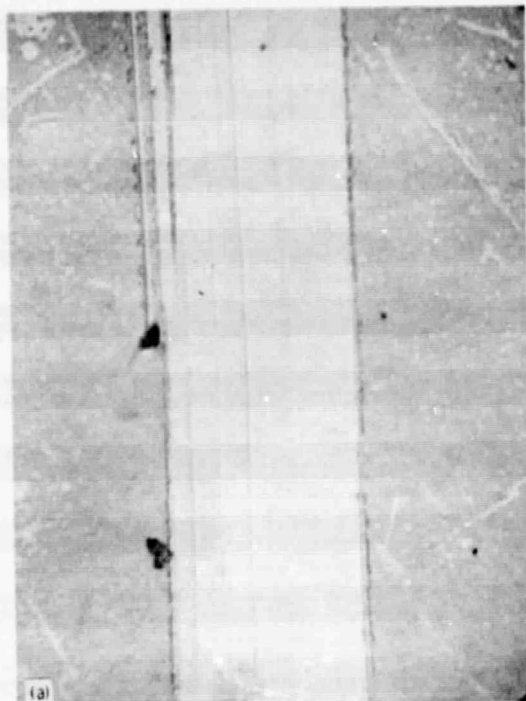


Figure 15. - Deformation tracks developed on a zinc (0001) surface in sliding contact with a ruby ball under a 200 gram load and in hexadecane.

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Figure 16. - Gold transferred to a clean silicon (111) surface after adhesive contact. Load, 30 grams; temperature, 23° C; pressure, 10^{-8} N/m².

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